Design and Implementation of High Pressure Systems

by

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Adrian Bejan

Thesis submitted in partial fulfillment of
the requirements for the degree of Master of Science in the Department of
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ABSTRACT

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Abstract

Hydrogen is arising as a potential fuel source due to its high mass-specific energy and wide applicability. However, hydrogen must first be pressurized before being implemented, causing a loss in efficiency and larger issues in implementation. Current processes produce hydrogen at low pressure and then pressurize the gaseous hydrogen with a compressor. Thermodynamic studies have shown that producing hydrogen in pressurized chambers could reduce the energy losses due to compression, raising generation efficiency. These projected gains are purely theoretical, however, and ignore practical limitations. The goal of this thesis is to design and construct a safe high-pressure hydrogen producing system at 5000 psi and to show the steps and considerations during this process.

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Acknowledgements

I thank Nico Hotz for guidance and direction in a time of confusion. Also I thank Andrew Schicho, for making sure I didn't mess up too many things on the way to the end.

1. Introduction to Hydrogen

In an ever-changing world, how power and energy is distributed and used holds weight with every aspect of life. There are many different media with which to transport required energy; some are ingrained into the everyday life, such as gasoline, wood, propane, and natural gas. Others are just beginning to be recognized, like compressed hydrogen, novel biomass fuels, and battery packs. When dealing with the transport of energy, the most commonly recognized idea is that of a fuel. Fuel, also known as an energy carrier, comes in many forms. Gasoline, coal, and natural gas are all examples of energy carriers that are encountered on a day-to-day basis in industrialized societies.

Fossil fuels are energy dense and therefore economically transportable. This is why the energy economy has evolved around using them for electricity generation, industrial applications, and personal transportation. It is well known that the drawbacks of these fossil fuels include their pollution of the environment and long-term sustainability issues. These concerns have spurred increased research into more sustainable and environmentally benign energy carriers such as batteries and hydrogen. Lithium electrical batteries have recently become a popular and successful energy carrier in personal transportation vehicles; however, they have a short life cycle and their disposal creates hazardous waste. Another new energy carrier which shows promise is

hydrogen. Its main benefits include its high mass-specific energy density, environmental neutrality, and its ease of integration with current fuel cell technology.

1.1 Hydrogen as an energy carrier

Hydrogen and its production are gaining recognition as a potential substitute to conventional fuels. Figure 1 shows both the volumetric and mass-specific energy density of many currently available energy carriers. It is important to note that hydrogen has the highest energy density in MJ/kg of all the energy carriers, both conventional and modern. Despite this, the figure also shows that hydrogen gas has low volumetric energy density (MJ/L) due to its gaseous form. Volumetric energy density is important, as it determines the space needed to carry the fuel in mobile applications. Gasoline, for example, has moderate volumetric and mass-specific energy densities, explaining its ubiquitous use as a transportation fuel. For example, one gallon of gasoline (3.785 liters), with a volumetric energy density of 34.8 MJ/L, contains 131.72 MJ of energy (Oak Ridge National Laboratory, 2014). In comparison, hydrogen at atmospheric pressure has a volumetric energy density of 1.005e-5 MJ/L (College of the Desert and SunLine Transit Agency, 2001). A gallon of hydrogen then contains 3.804e-5 MJ, about 3.48e6 times less than gasoline. However, pressurized hydrogen can greatly reduce this disparity. The Department of Energy has several pressure standards for hydrogen, ranging from 25 MPa (3.6 kpsi) to 70 MPa (10 kpsi) (U.S. Department of Energy, 2011). Hydrogen pressurized to 35 MPa (5 kpsi), also known as H35, is

considered a baseline pressure for transportation purposes. At this pressure, the energy density rises to 2.7 MJ/L, making a gallon of gasoline contain only 12.9 times more energy. This trend of pressurization can be pushed until hydrogen turns liquid, resulting in an energy density of 8.5 MJ/L (College of the Desert and SunLine Transit Agency, 2001). This leads to a factor of 3 difference in volume needed when compared to gasoline, making liquid hydrogen feasible. However, tanks for liquid hydrogen require special conditions such as cryogenic cooling, making them somewhat impractical for transportation.

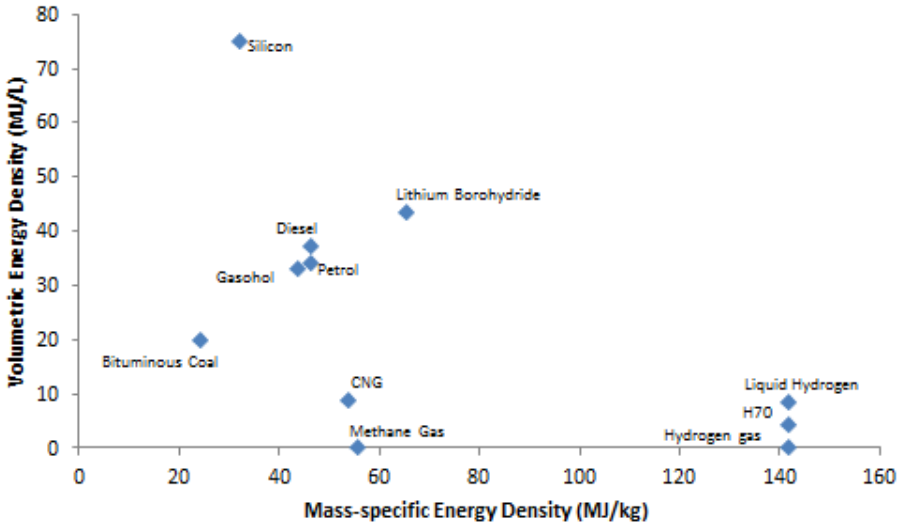

Figure 1: Plot of energy densities of common energy carriers. Note hydrogen's place in the far right.

By these standards, hydrogen must undergo compression before it can compete as an energy carrier with conventional fuels. Pressurizing gases can be difficult due to their high compressibility and volatility. In most cases the process of compressing hydrogen is done after the hydrogen is generated, decreasing the overall efficiency of

conversion. In response, this thesis shows how to design and establish a working system for hydrogen production in a high-pressure environment. Based on the work of Onda, LeRoy, Appleby and Laoun, such designs can lower losses from pressurization and increase hydrogen's practicality as a replacement for hydrocarbon fuels.

1.*2 Current hydrogen production and research*

The U.S. Department of Energy recognizes hydrogen as a potential hydrocarbon replacement and assembles a yearly progress report on current hydrogen research. The report covers issues including hydrogen production, storage, and safety standards. Despite the advances in hydrogen production technology, steam reforming is still the industry standard for hydrogen generation. This process involves converting fossil fuels, particularly methanol or natural gas, into hydrogen through high temperature steam reformation. Steam reforming produces hydrogen efficiently by heating a reactor chamber containing a catalyst which breaks the hydrocarbon chains. The result of this chemical reaction is primarily hydrogen, carbon monoxide, and carbon dioxides. Steam reformation can produce hydrogen from highly energy dense liquid fuels such as methanol, eliminating the need for pressurized hydrogen tanks in fuel cell cars. However, this process currently depends mostly on fossil fuels, a finite resource with long-term sustainability issues. It also has challenges associated with separating the product gasses so as not to poison the fuel cells with carbon monoxide and does not reduce greenhouse gas production.

Department of Energy targets for the future include the development of new technologies which can replace steam reformation of fossil fuels and make hydrogen competitive with conventional fuels in the energy market. In the most recent progress report, these technologies included electrolysis, solar thermochemical, photoelectrical, and biological systems for hydrogen generation (U.S. Department of Energy, 2013). Hydrogen production solutions are being developed outside of the DOE as well. Specifically, the International Journal of Hydrogen Energy releases several issues a year, collecting papers to show innovation in hydrogen's use as a potential fuel. A relevant example comes from the 2013 volume, where a group of researchers investigated how fire in hydrogen fuel cell cars could propagate due to high-pressure tanks (Zhen, 2013). Of these emerging technologies, the simplest and most straightforward way to produce hydrogen is water electrolysis.

1.3 Electrolysis of water

Water electrolysis is the production of hydrogen and oxygen gas by simple disassociation of the water molecule by applying the electrical potential needed to break the chemical bonds. Water electrolysis requires an input of 1.48 V to occur under standard atmospheric conditions (Leroy, Bowen, & Leroy, 1980). This voltage, or reaction potential, drives the disassociation of water. While producing hydrogen in water is simple in this manner, there are various ways of achieving the reaction potential with varying degrees of efficiency. A commonly used method of electrolyzing water is

through a proton exchange membrane (PEM). PEM electrolysis is the application of a solid polymer electrolyte (SPE), which uses the input of electrons to dissociate water and separate hydrogen gas from the oxygen byproduct. This process seems promising as an emerging technology due to its high output gas purities and high current density potential. Unfortunately, PEM membranes are highly sensitive to pressure, as the membranes must be extremely thin in order to operate effectively and are expensive to produce. Current state of the art technology PEM stacks aim to keep pressure equal on both side of the membrane while reinforcing them with expensive and intricate frames and backings (Marangio, 2009).

To avoid these complications this thesis will focus on traditional electrolysis, which requires just two electrodes submerged in water with a potential difference applied across them. To facilitate the reactions, the electrodes act as oxidation and reduction sites where hydrogen (and oxygen) is produced. The material chosen for the electrodes varies depending on the demands of the system. The topic of electrode material choice itself is widely researched. While platinum is considered an ideal due to its high conductivity and inert nature, it is too expensive to be realistically implemented. Stainless steel and other high nickel content alloys have been proven as suitable substitutes due to their high corrosion resistance and availability (Zhang, 2010). In addition, the corresponding spacing and shaping of the electrodes can also affect process efficiency (Ohnishi, Osawa, Tanaka, & Wakizaka, 2005; Nagai, Takeuchi, Kimura, &

Oka, 2003). Electrolysis can be accelerated by the addition of electrolytes to the solution, as pure water is, for all intents and purposes, an insulator. The current industrial standard is the use of alkaline solutions in the water. Alkalides were chosen for their ability to carry electrons through the solution while not reacting at the electrodes keeping the chemistry of the product gasses pure. Most alkaline solutions call for a hydroxyl combination, but others have insisted that using sea water could prove simpler, cheaper, and more effective (Abdel-Aal, Zohdy, & Kareem, 2010). While this process lacks the benefits of PEM electrolysis, it has potential to increase efficiency in post processing of hydrogen. As discussed before, in order for hydrogen to be practical, it must be pressurized. Electrolysis can be achieved even in pressurized environments. This means the product gas is pre-pressurized decreasing and in some cases negating completely the need for a secondary gas compressor. This process increases the overall efficiency of high-pressure hydrogen production in two ways. First it eliminates the post production pressurization, and second it is thermodynamically favorable as compared to traditional atmospheric electrolysis (Onda, Kyakuno, Hattori, & Ito, 2004; Appleby, Crepy, & Jacquelin, 1978).

1.4 High-pressure hydrogen generation

The pressurization of hydrogen is one of the few issues keeping it from becoming a more widely used fuel. Pressurization is required to give the hydrogen a useful volumetric energy density, a trivial thought for most conventional fuels. Currently,

hydrogen is generated and then pressurized via a compressor, an inefficient process due to the compressibility of gas. However, pumping water into a pressure vessel and subsequently up to the desired output pressure is an easier and more efficient process. According to theoretical models, water electrolyzed at 400 atm (~6000 psi) starts to achieve higher efficiencies than compressing post-production (Laoun, 2007). To achieve these pressures reasonably, fundamental electrolysis stands as the simpler solution, despite its weaknesses when compared to PEM electrolysis. The Department of Energy has funded research of a stacked PEM electrolysis system for home use designed to use 5000 psi water, but it is extremely costly and generate very little hydrogen (Norman & Hamdan, 2013). In addition, fundamental electrolysis can benefit from the high pressure during electrolysis, as the pressure creates smaller formation sites on electrodes keeping the bubble fraction low (Appleby, Crepy, & Jacquelin, 1978).

1.5 Goals and objectives of thesis

Current research on high-pressure hydrogen production avoids some interesting questions. While the Department of Energy's stacked PEM electrolyzer has achieved hydrogen production at 5000 psi and vies for 10,000 psi in continuing years, high-pressure fundamental electrolysis has been generally ignored. Most research has chosen to stay theoretical, giving thermodynamic potentials of ideal reactions and the potential gains from high-pressure systems. Others have attempted fundamental electrolysis at higher pressures, mostly through alkaline solutions, but have not attempted the

pressures required for viable efficiency increases (Janssen, Bringmann, Emonts, & Schroeder, 2004759-770). This comes with good cause, as producing hydrogen at high pressures is both difficult to accomplish in a physical system and is dangerous if handled incorrectly. In fact, the Department of Energy progress report goes into great detail about safety and standards. More specifically, these standards highlight the risk behind hydrogen production, specifically the materials susceptible to hydrogen embrittlement and the behavior of hydrogen when released at high pressure (James, 2013).

The objective of this thesis is to discuss the system design and safety of the high-pressure hydrogen production system at Duke's Thermodynamics and Sustainable Energy Laboratory (T-SEL). Currently, T-SEL is researching the potential benefits of hydrogen production by traditional electrolysis at high pressures. The goal is to achieve H35 pressure standards with pure water as a baseline for future salt water electrolysis experiments. As a result, T-SEL has constructed a physical system to accommodate the pressures and chemical conditions needed for those standards through various purchased and custom made parts. Specifically, the design contains three sub systems: electrical requirements, pressurization process, and flow safety and control. Through discussion of each piece and its function, this thesis will bring light to the needs of such systems and explore its potential for the production of hydrogen at high pressures

2. Electrical system

Hydrogen generation requires an input of energy, or electric potential, to occur. Hydrogen is produced through the disassociation of water via this electrical potential. During the process, two separate half reactions occur, given in the following equations.

Cathodic reaction: $2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$

Anodic Reaction: $2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4\ e^-$

In these reactions, the total potential is 1.48 V and serves a baseline voltage needed to generate hydrogen. Given the low conductivity of pure water, an electrolyte must be used to maximize use of the input electric potential. Sodium chloride shows promise both for its high conductivity and easy accessibility from ocean water. With the additional components in the reaction, the reaction equation changes to a chlorine gas producer.

$$2\ NaCl + 2\ H_2O \rightarrow Cl_2 + H_2 + 2\ NaOH$$

In industry, this reaction is widely used for the production of chlorine with hydrogen and caustic soda considered as positive saleable byproduct. Consequently, the use of salt water as the working fluid should be handled with care, as the chlorine gas produced is toxic. To give illustration to the electrical system, Figure 2 gives a simplified schematic of how the electrical system was designed.

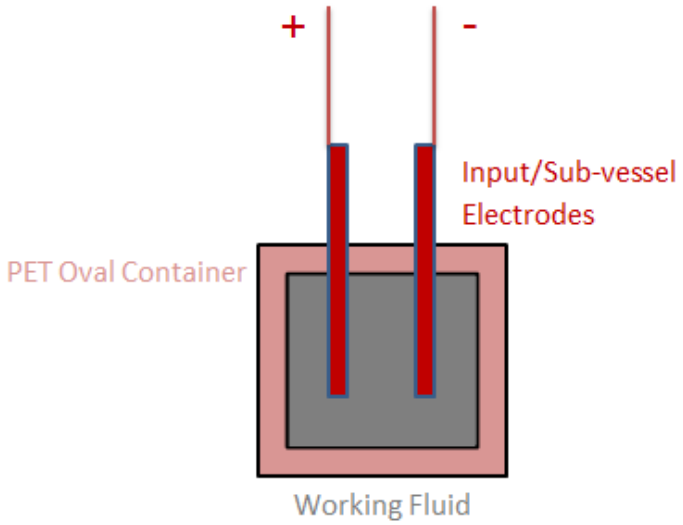

Figure 2: Simplified schematic of electrical system. Color coded to red.

2.1 Input electrodes through pressure vessel

Due to the limited size of our reaction chamber, electrodes were inserted through the top of the pressure vessel. These electrodes carried the voltage to the container's own set of electrodes, which act as the sites of hydrogen and oxygen generation. The electrodes were machined to ¼" diameter and then press fit into plastic sleeves to electrically insulate them from the pressure vessel. To seal them from the outside, they were inserted into glands purchased from Conax, which are discussed further in Section 3.2.2.3.

2.2 Sub-vessel electrolysis parts and set up

The design of the electrical system turned out to be more difficult than anticipated. Originally, the idea was to generate hydrogen in the pressure vessel itself,

allowing for easy pressurization and facilitating continuous production. After testing the electrical conductivity, however, it was found that the voltage was not only going through our electrodes, but also through the vessel itself, charging it with about 10% of the input voltage. This voltage leak posed two serious problems. First, a charged vessel system could potentially shock our precision pump, changing its input or damaging it. Second, this meant that hydrogen could potentially form on the walls of the vessel instead of the anode, accelerating corrosion and hydrogen embrittlement. To counteract this problem, a smaller, compressible vessel was implemented within the larger vessel to house the reaction in a conductive but isolated volume.

2.2.1 Container

The container was designed to hold the working fluid during electrolysis and to electrically insulate the electrolysis process from the rest of the pressure vessel. Due to the limited space within the pressure vessel, jars, deemed such for their small height but high width, were considered the most appropriate option, as they could fit the most easily into the vessel while maximizing the amount of working fluid available. The material also was under consideration due to its need to be both electrically insulating and ductile enough to absorb the high pressure without fracture

Many jars were purchased to test their suitability to the pressure system. Ultimately, a Powell oval jar was chosen due to its high volume to entry diameter ratio.

The jar selected was made of polyethylene terephthalate (PET) due to its flexibility. Figure 3 shows the jar chosen.

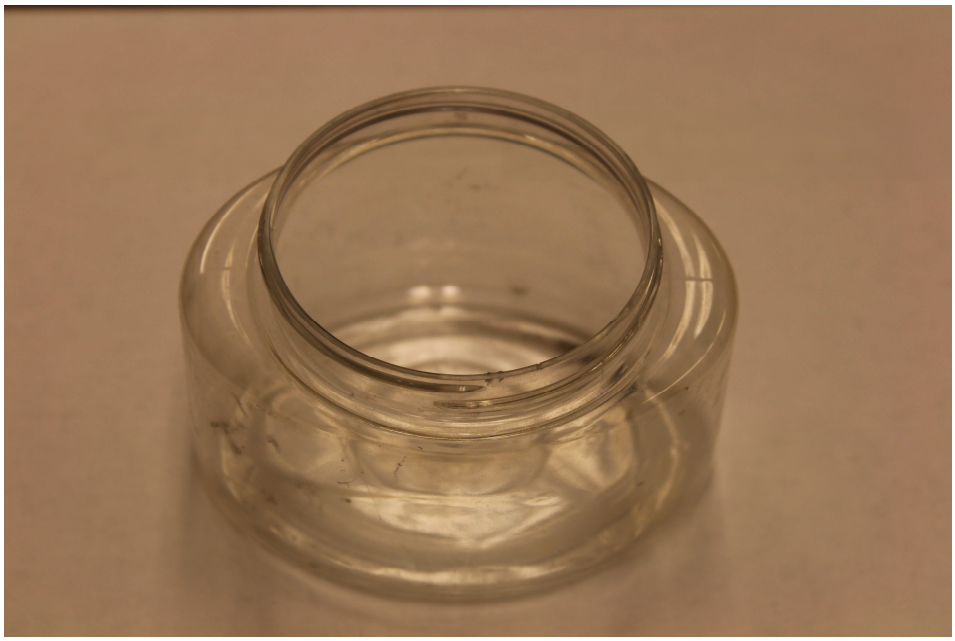

Figure 3: Flexible container for sub-vessel.

2.2.2 Cap

The cap's sole purpose was to seal the jar from any leakage, so that the electrolysis could run safely and consistently. A size 13.5 rubber stopper was chosen as the cap. Due to height restrictions, the stopper was sliced in half horizontally, reducing the height from 1.365" to .6825". Through the top of the cap, three holes were drilled out. Two of these were designed for an interference fit with the two input electrodes, using the slight interference as an electrical and fluid flow seal. The other drilled hole served as an outlet for the hydrogen gas produced. This hole was tapped with 1/8" NPT threads to ensure all gas flows through the outlet and not into the pressure vessel.

2.2.3 Sub-vessel electrodes

Due to the nature of an electrolysis reaction, the material chosen for the hydrogen generation site played a significant role. Many metals under the reaction will corrode away as hydrogen is produced. Copper, for example, while highly conductive, corrodes rapidly at the anode when subjected to electrolysis. High corrosion impedes the reaction and possibly poisons the working fluid, making hydrogen generation decline over time. Therefore, a material with both a high anodic and cathodic potential with low corrosion rates had to be found and implemented.

Ultimately, 316 stainless steel was chosen as the working fluid electrode. While there are more ideal metals to use in electrolysis, such as platinum, 316SS was the easiest to acquire and construct. Two 3/8 inch diameter rods were inserted through the rubber cap and into the sub vessel. To input the voltage needed to drive the reaction, these rods were connected to the electrodes going through the vessel top, discussed in Section 2.1.

Electrolysis reaction rates are highly determined by the amount of current flowing between the cathode and anode. Faraday's 1st law of electrolysis explains this phenomenon: the mass of a substance altered at an electrode is directly proportional to the electricity transferred to it. Specifically, during constant current cases, the equation becomes the one shown below (m = mass produced, I = current, t = time, F = Faraday constant, M = molar mass and z = number of valence electrons).

$$m = \left(\frac{I * t}{F}\right)\left(\frac{M}{z}\right)$$

To standardize electrical current values over different types of systems, the input current is reported as a current density over the area of the electrodes. In the sub-vessel electrodes, 4 cm by 5 cm rectangles of #60 316 stainless steel mesh were attached in parallel onto the inserted rods. This specific mesh was chosen based on the research presented in the International Journal of Hydrogen Energy, highlighting its many geometrical advantages (Zhang, Merrill, & Logan, 2010). The mesh increases the surface area as compared to a large flat surface as the reaction will occur in the small gaps given between each wire in the mesh. These gaps also create more formation sites for the hydrogen bubbles, increasing the rate of production. Finally when held vertically the bubbles that release their hold on the mesh create a fluid shearing effect that increases flow through the mesh and knocks off more bubbles. This lowers the bubble fraction and speeds the rate of reaction causing an increase in gas production.

2.2.4 Outlet for produced gas

In this design, the hydrogen production was designed to be created in batch loads. Although the ideal system would produce gas continuously, production in this way is extremely difficult to maintain with two fluids of different purpose and composition in the system. To protect from potentially dangerous situations, such as the electric charge leaking into the pressure vessel system, current batch production was satisfactory for now. With this in mind, the outlet for the hydrogen from the sub-vessel needed to be designed to open only when the experiment was over and pressure was

released from the system. The outlet contained a T-junction with two one-way valves. The perpendicular side of the junction faced the pressurizing fluid and a-one way valve pointed into the junction was attached via 1/8″ NPT threads. One parallel side fit into the rubber cap of the sub-vessel with a one way valve coming out of the cap into the junction, also via 1/8″ NPT threads. The last end of the junction fit into the outlet of the pressure vessel system with a fabricated nozzle to direct the hydrogen into the outlet. These valves allowed the entire system to maintain pressure equilibrium without the mixing of the working and pressurizing fluids. An added benefit of the outlet assembly was that produced gas was directed straight to the outlet so none was lost in the pressure system. The T-junction, along with the rest of the cap, used is shown in Figure 4.

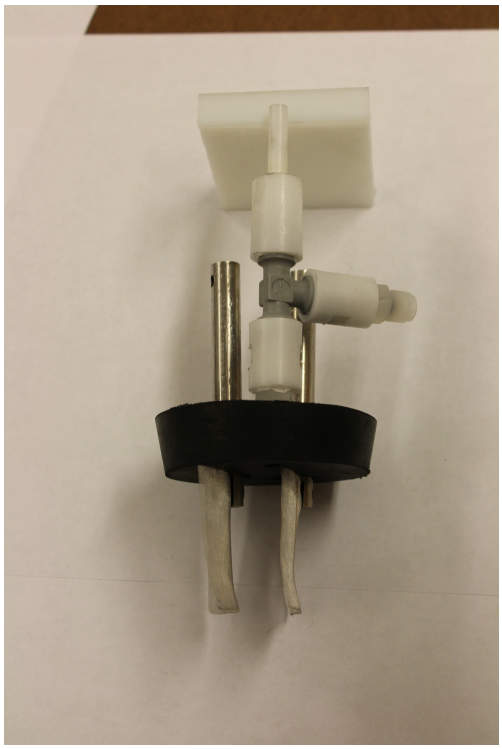

Figure 4: Sub-vessel cap with electrodes and T-junction attached. Working fluid and pressurizing fluid cannot mix until pressure is released.

With this set up, pressure could equalize during initialization and depressurization without cross contamination between the vessel and sub-vessel. The one-way valves have a minimum activation pressure of 2 psi and fail at 250 psi. While the pump was running during initialization, the fluid around the sub-vessel pressurized, applying the same pressure to the sub-vessel due to the incompressibility of water and the flexibility of the sub-vessel's container. The perpendicular one-way valve also allowed the pressurizing fluid to move through the outlet, thereby pressurizing the outlet water without entering the sub-vessel's container and not crushing the plastic T-

junction assembly. No working fluid left the sub-vessel into the output line during the set-up, only pressurization fluid.

3. Pressure vessel system

The core component to hydrogen production at high pressure is the pressurizing vessel. The vessel had to be able to resist cyclic loads of pressurization, be resistant to numerous forms of corrosion, and be sealed well enough to ensure no water or gas leakage at pressures up to 5000 psi. Due to the complexity and potential safety hazards of the vessel, it was designed and fabricated by HiP via a special order. The fabricated piece was ANSI certified before being delivered, assuring safety and reliability in pressurization. The simplified schematic of the pressure system and the electrical system's place inside is shown in Figure 5.

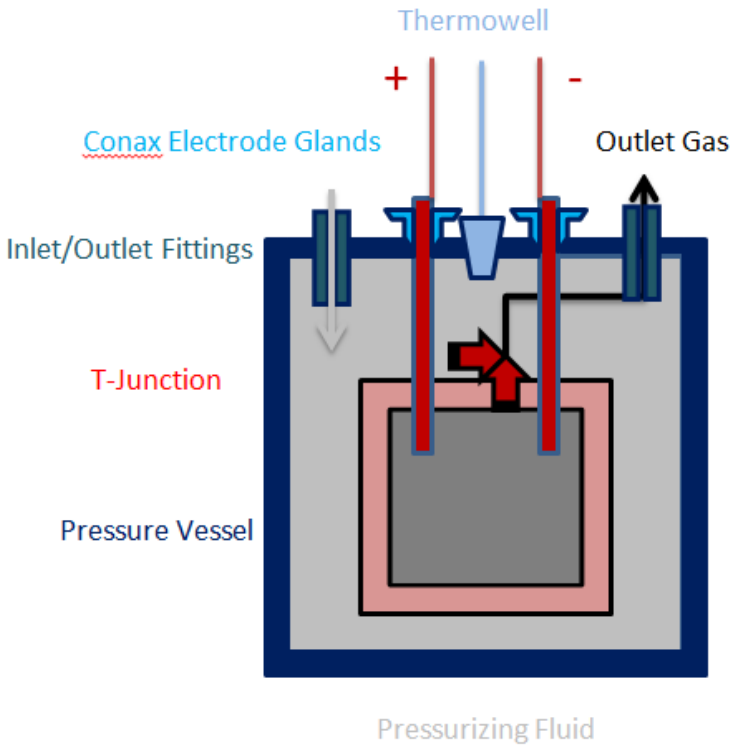

Figure 5: Simplified schematic of pressure system with embedded electrical system. Pressure system color coded to blue.

3.1 Base

The vessel was cylindrical in shape, with a concentric interior that tapers to a point at the end, giving solid one inch walls and large reinforcement at its bottom. The vessel was made of solid 316 stainless steel due to its high corrosion resistance and strength. In addition, because of the cap's size and weight, a superstructure was fabricated to give support for lifting and leverage during tightening set up and tear down of the system. The superstructure was made with aluminum extrusion pieces ordered from *80/20 Inc.* due to their easy assembly and strong support. The

superstructure gave support to the base from sliding or spinning during set up times and allowed for the implementation of a pulley system to secure the cap onto the base (discussed in Section 3.3).

3.2 Top

The part of the pressure system deemed the top connects into the base through an O-ring. The top served two functions: sealing the pressurizing fluid in and serving as the port for inlets and outlets. The top, like the base, was designed to resist corrosion and cyclic high pressures. It was completely fabricated of 316 stainless steel. A picture showing the top of the pressure vessel system is shown in Figure 6.

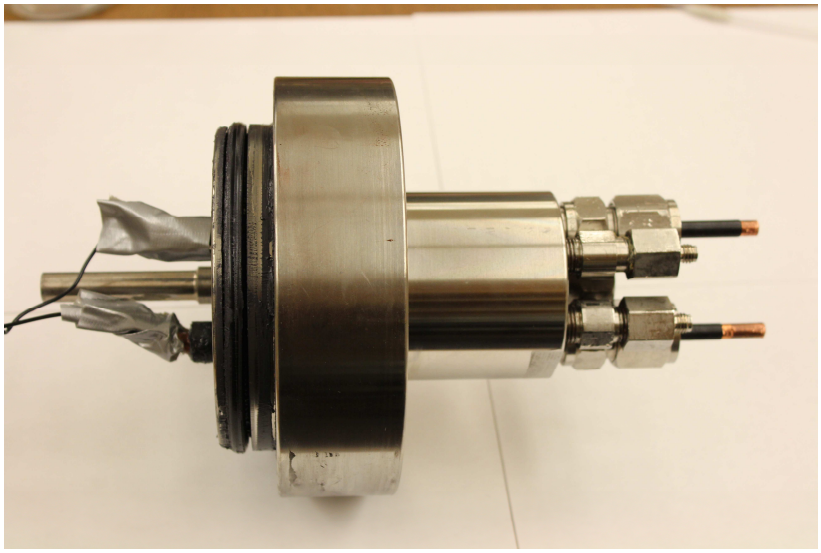

Figure 6: Fully assembled pressure vessel top.

3.2.1 O-ring seal

HiP's design implemented an O-ring to seal the system and hold pressure. The top had an O-ring groove fabricated in it to facilitate this. Due to the size of the O-ring

required and the amount of shear force required to insert it into the base, a special lubricant was necessary during set-up.

3.2.2 Designed inputs and outputs

As requested of HiP in our design needs, the top of the vessel was built with five inputs into the pressure vessel. Oriented a circle around the top, one hole was designed for the thermowell; two, for the flow of water and gas in and out of the vessel, respectively; and two, for the electrodes to be inserted as discussed in Section 2.1. Figure 7 shows the designed inputs and outputs and their configuration on the top.

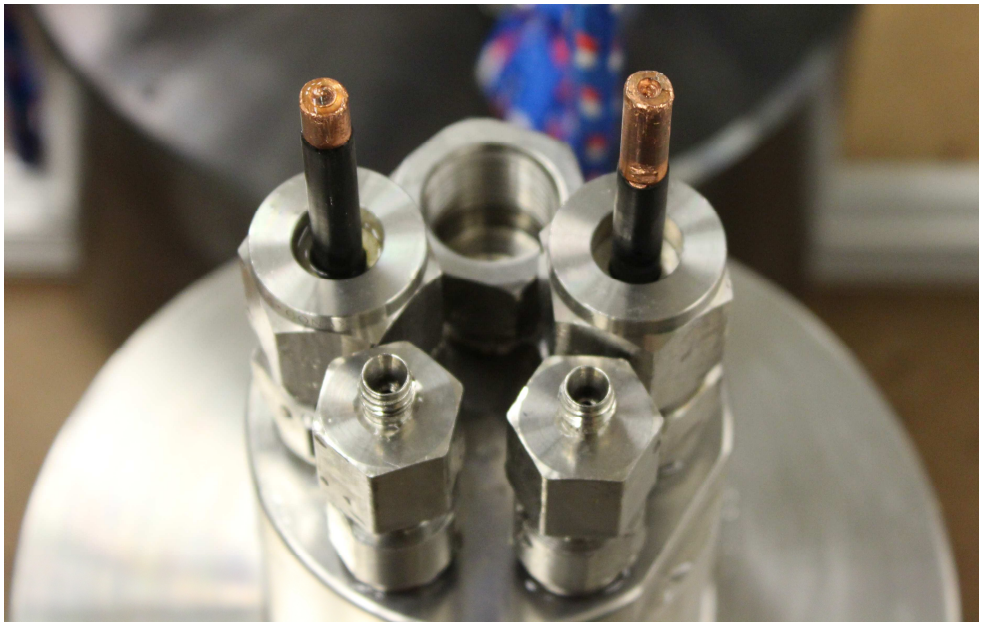

Figure 7: Overhead view of pressure vessel top. Clockwise from 12 o'clock: Thermowell, positive electrode, water outlet, water inlet, negative electrode.

3.2.2.1 Thermowell

In the top of the pressure vessel, a ½" NPT hole was tapped in for the thermowell to enter. A thermowell input was designed into the system for two specific

reasons. First, the temperature had to be measured to compare sets of data for electrolysis. Temperature has an effect on the rate of reaction, so a baseline temperature needed to be measured to test system efficiency. Second, the system was rated by HiP for temperatures below 100 degrees Fahrenheit. Higher temperatures could compromise the system and therefore must be measured to ensure system integrity and safety. In the system proposed, a series 445S thermowell was purchased from Omega.

3.2.2.2 Water pressure inlet and outlet

The purchased vessel was designed from one of HiP's high-pressure products and simply had slight variations made to accommodate the electrolysis to occur inside. As such, the vessel was actually designed for pressures up to 7500 psi, whereas the system described here only needed 5000 psi. Because of the base model's high psi tolerance, it was designed to have special high-pressure fittings (20,000 psi rated) to ensure no leakage at the inlets and outlet points of the system. These special fittings added a conical nozzle to the end of every fitting and required they be three piece fittings specifically designed for ultra-high pressures. This posed issues in the design, as none of the other parts of the system had this designed in and the conical add-on required special, non-flexible tubing. So, as a response to this, a fitting that transferred the ultrahigh pressure conical fitting to the system standard was designed and fabricated. Two fabricated conversion fittings were attached at the water input and

output, which then led to the flow system. Both the conversion fittings and the flow system are described in more detail in Section 4.2.

3.2.2.3 Electrical system inputs

As discussed in Section 2.1, two electrodes needed to come through the top of the system into the working fluid to drive the electrolysis reaction. The copper input electrodes were sealed into place by glands designed by Conax. The Conax gland used was a PG4-275-A-L, meaning, in order, bore size, diameter of tube, threaded cap style and "Lava" composite ferrule. These glands use multiple pieces to squeeze onto the electrode, ensuring no leaks and keeping them in place. Figure 8 shows Conax's depiction of how the PG4 glands operate.

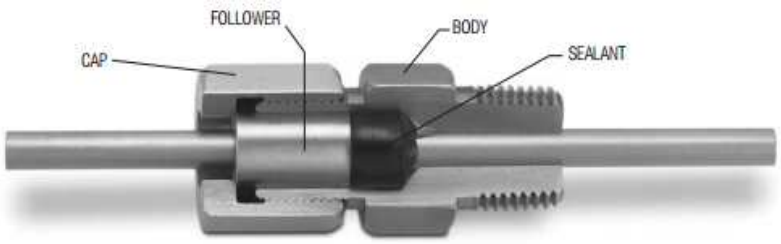

Figure 8: Technical drawing of a Conax gland for the electrode. Pressure rating from vacuum to 10,000 psi.

First, the body screwed into the top with 1/2" NPT threads. This body piece houses the special ferrules in the gland and connects it to the system. Into this base, two ferrules are placed, one made of steel (follower), the other a special composite (sealant). According to Conax, the sealant used is called "Lava" and is specially designed for higher-pressure systems. Both the metal and Lava ferrules had a custom sized hole cut

out of their centers for the electrodes to fit through so that when the whole gland is assembled, they create a surface-to-surface seal. Finally, the cap screwed into the outer threads of the base, creating the pressure needed for the gland to seal.

3.3 Cap

To ensure the top stayed onto the base and kept the O-ring seal, an additional cap was placed above the top. This massive piece slides through the extruded center of the top and threads onto the base, leaving the ports in the top exposed while securing the top. The threads used for the cap and base are large square threads that wear easily due to the weight of the cap. To counteract this wear, copper-based lubricant was applied. In addition, to take stress off the base, a pulley system was designed and installed into the super structure holding the base. The cap was lowered into position and rotated onto the threads with no friction, using the pulley and springs as a suspension system. This process usually required two people to operate; one lowering the pulley at a steady pace, the other rotating the cap onto the base. Figure 9 gives a simplified cross-sectional view of the three major pressure vessel components and how they fit together.

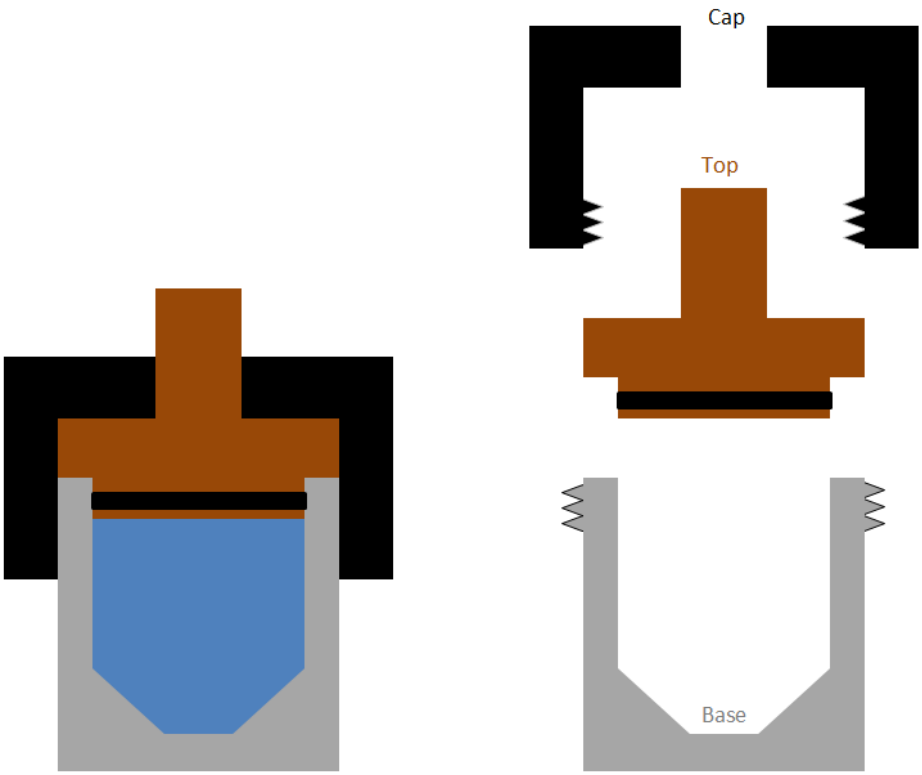

Figure 9: Simplified, two-dimensional construction of pressure vessel. Does not include electrolysis components.

4. Piping and flow system

The piping system was designed to get the working fluid into the pressure vessel and pressurize the system. Pressurization of the system was a fragile and dangerous process, so many precautions were taken and implemented in this part of the system. Due to the batch production nature of the entire system, this specific part only had to account for the input of pressurizing fluid into the vessel and a gas-water mix out of the outlet. To illustrate the flow system as a whole before going into detail, Figure 10 shows the simplified schematic of how the system operates.

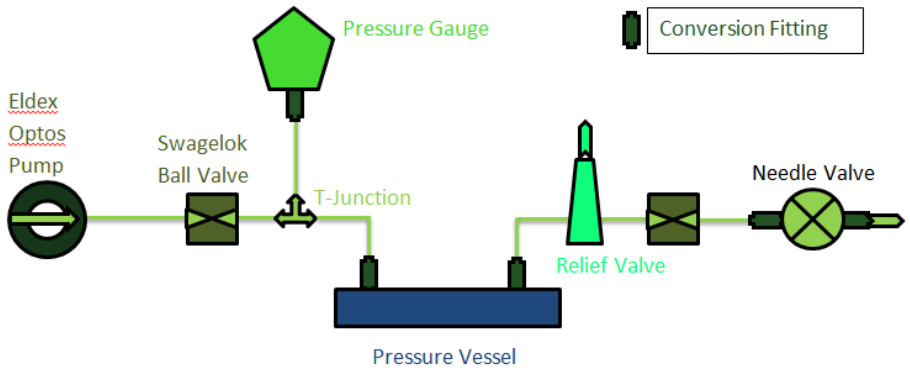

Figure 10: Diagramed of flow system. Color coded to green.

4.1 Parts and specifications

4.1.1 Pump

To pressurize our system during initialization, an Eldex model 2SM Optos metering pump was used. Optos metering pumps are specially designed for high-pressure applications with a range of different fluids. The Optos pump offered a max pressure of 6000 psi and a max flow rate of 10 mL/s, both high enough for maximum

testing conditions. However, due to the delicate nature of the pump, several precautions were taken to ensure long usage life. This involved degassing the pressurization fluid before putting it through the pump and extensive cleaning after usage. While these served as minor inconvenience during set up and tear down, the pump was able to get the system up to 5000 psi consistently with little to no difficulty and was very reasonably priced.

4.1.2 Tubing and connections

Swagelok provided the appropriate steel tubing for our flow system. The specific part number for this piece was SS-T2-S-028-20. This tubing was 1/8" outer diameter with a 1/16" opening. The tubing was also comprised of 316 stainless steel for the corrosion resistance. This tubing was chosen due to its flexibility and adaptability into the system. In conjunction, 316 stainless steel female connectors were used at each fitting point. The specific part number from Swagelok for these connections was SS-200-7-4. These female connectors fit around the 1/8" tubing and connected via 1/4" threads. Connectors were attached to the tubing via Swagelok's two-ferrule mechanical grip design. These proved useful for easy set up and take down, but were highly subjective to wear after multiple tests, over crushing the ferrules with time.

4.1.3 Pressure gauge

With the vessel, HiP supplied a standard pressure gauge. From their catalog, its serial number is 4PG10. This gauge can be used up to 10,000 psi with marks every 100

psi, accurate enough for testing at the goal of 5000 psi. This connection was set up in the T-junction perpendicular to main flow and was somewhat above the system height wise. This means that air could possibly have been trapped in the pressure gauge, adding small amounts of time to pressurization. In the future, the pressure gauge may be mounted elsewhere as the Swagelok fittings make the system modular.

4.1.4 Ball valves

Two Swagelok ball valves were installed to isolate the system during testing to reduce wear on the pump and needle valve. Specifically, the valves were SS-4SKPS4, meaning they were made of 316 stainless steel and for 1/4" fittings. The SK series from Swagelok is designed for pressures up to 6000 psi and operates with high flow capacity. As shown in Figure 10, these valves isolated the system during electrolysis. The end ball valve was shut during pressurization and once the desired pressure was reached, the pump was turned off and the initial ball valve was shut.

4.1.5 Relief valve

Due to the safety limits of our vessel, a relief valve immediately attached to the outlet was a necessity. The blowout valve supplied by HiP, serial number HiP-10RV, was designed to handle pressures in 1000 to 10,000 psi range. Because most pieces in the system were rated to only 1000 psi above testing pressure, this valve acted as the emergency safety outlet. The relief valve would be set to a certain pressure, in the case of our vessel, 5000 psi, and any pressure in the system exceeding this would be expelled

by this valve. While it serves no core purpose to the process itself, the relief valve was vital to the safety of the system and a necessary part to a potentially volatile system.

4.1.6 Needle valve

To control the flow out of the system, a high-sensitivity needle valve was situated at the end of the system. This needle valve was supplied by HiP, serial number 30-11HF4. The specific needle valve was able to handle pressures of 30,000 psi. The sensitivity of the needle valve allowed a smooth continuous flow of hydrogen to be measured by a flow meter. However, due to its high pressure tolerance and design, it had the ultrahigh pressure inputs as well. As a result, custom fittings were fabricated and attached to the valve's input and output.

4.2 Custom fitting design and fabrication

When the pressure vessel system was ordered from HiP, the designed pressure limit for the system was 7500 psi. While the experiments done and pressure goals were nowhere near that pressure, it was still the most simple and easily obtained vessel available. Because of this high pressure tolerance, several of the pieces sent by HiP, including the vessel, piping, joints and needle valve, were designed with a high pressure nozzle fitting. The expected use of this fitting involved using rigid pipe with matching conical shapes at each end and two-piece fittings for each direction change and input. While this design ensured safety at ultrahigh pressures, it was impractical to consider for the designed system, both in implementation and financial terms. The resolved

solution was to design and fabricate fittings that would replace the presented solution in a timely and cost-saving manner.

4.2.1 Design parameters and analysis

To replace the stiff tubing suggested with the quick connect set up discussed in Section 4.1.2, each connection needed to fit to the new standard. To convert from the 1/8" tubing to inlet and outlets, Swagelok provided converters that gave 1/4" NPT female threads for the replacement to fit into. The other end needed to fit into the special, ultrahigh pressure fittings with the conical shape while using 5/8" straight threads. The solution was to cut out the need for the multiple piece fitting by combining the conical nozzle, threading and conversion threading needed for the Swagelok. As a result, the replacement fitting was designed with four parts, all to be fabricated as a single piece.

Since this part was designed and manufactured solely by the T-SEL lab and was not certified by any engineering body testing, its safety was paramount. As a result, the design was transferred into ANSYS and Solidworks to perform stress analysis on them before fabrication. ANSYS was first used to test for the worst-case scenario in a fitting. ANSYS was chosen due to its high accuracy and customizability in mesh size for internal stresses.

The worst-case scenario in these fittings would be fluid back up in the fitting, essentially pressurizing the fitting alone. For this analysis, a two-dimensional cut away

of the piece was modeled and meshed. A force of 5000 lbs was applied at all points inside the fitting, as if the system had reached its max force in the fitting. Figure 11 shows the resulting analysis.

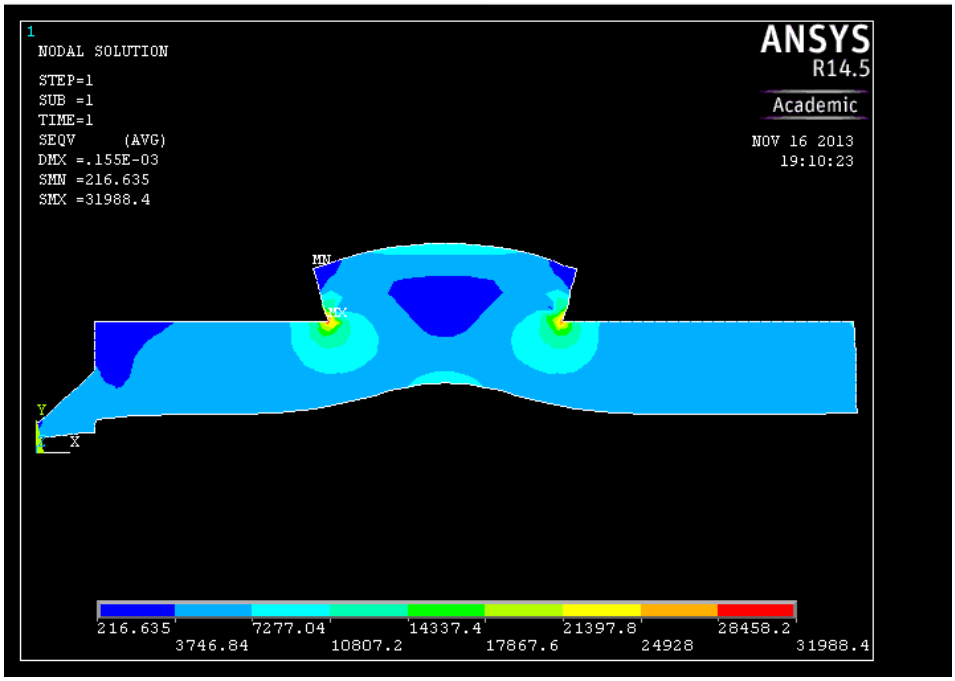

Figure 11: ANSYS stress analysis of 2-D internal cut of designed fitting.

As shown in the analysis, the Von Mises stress in the system was calculated to be 32,000 psi. This max, however, takes place at a sharp corner that was avoided during fabrication by rounding it with a 1/32" radius relief. When considering this against the yield strength of 304 stainless steel, 30,000 psi, a potential blockage in the system could force the fitting to yield. While this needed to be considered for the safety of the system, the stress applied in this analysis turns out to be around 8,500 psi, showing that the piece can stand up to the pressure needed by the system with a 1.5 safety factor.

To get an idea of how the piece as a whole would actually react under normal pressures, the model was then taken into Solidworks and analyzed there. Solidworks provided a better three-dimensional view on the piece while under normal stresses. In the following stress analysis, the high end pressure of our system, 5000 psi, was applied to the interior while fixing the position of the threaded pieces and the outer part of the nozzle.

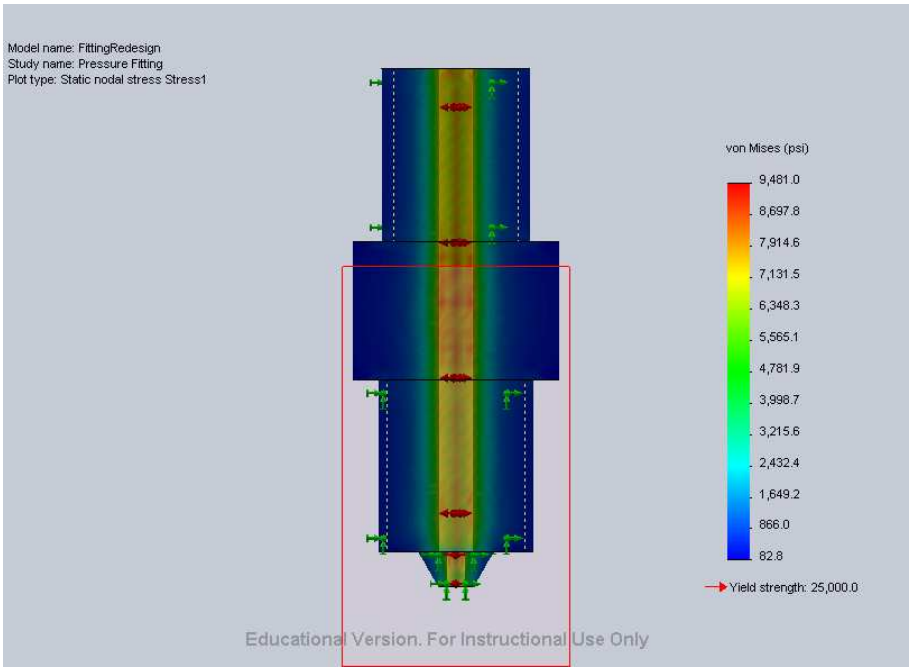

Figure 12: Solidworks stress analysis on designed fitting. Dotted lines represent threads.

Figure 12 shows that not only does the piece undergo minimal stress, but also that there are no severe stress concentration points. The conical piece also experiences minimal stress, meaning the integrity of the fitting would not be compromised over

time. This was a major concern, as the high-pressure nozzle fitting required a perfect fit to operate without leakage and would create the best seal for these critical points.

4.2.2 Fabrication

The replacement fittings underwent several phases of fabrication. The first set of fabrication was done with 316 stainless steel, both to match the rest of the system in corrosion resistance and toughness and to eliminate all issues with dissimilar metals touching. However, this proved to be difficult, as the high hardness of 316 stainless steel broke several dies in the threading process and took a significant amount of time to turn down in the lathe. After two unsuccessful attempts at fabricating the piece with 316 SS, it was decided that a new, softer metal would have to suffice. 304 stainless steel was chosen for its equally high stress tolerance and easy machinability. After several attempts at getting the perfect ratios for the conical nozzle and the 1/4" NPT threading, the five required fittings were made and installed.

Figure 13: Picture of a sample fabricated fitting. From left to right: high pressure nozzle, 5/8″ straight threads, spacer for wrenching, ¼″ NPT threads.

5. Results and Discussion

5.1 System integrity

The pressure vessel went through many iterations before being able to hold the pressure required. Most of this came from the inhomogeneity of the parts. Pieces from different companies did not always match up perfectly and solutions were devised to bridge those gaps. In order to convey the issues faced during design and fabrication of such a system, a few examples and their solutions are presented in this section.

The first major issue came from the ultrahigh pressure fittings discussed earlier. The tube needed to fit these connections was too rigid and difficult to work with. Initially, hydraulic piping was considered due to its high adaptability. Also, the endings for most hydraulic piping were diverse enough to easily fit into a designed conversion fitting. However, the pipe diameters necessary to hold the pressure needed were too high, eliminating it as an option.

Once this issue was resolved and the flow system was set in place, the issue of electrolysis inside the system arose. At the start, the design simply had the working fluid inside the pressure vessel with the reaction potential coming straight through the electrodes. This posed several issues, however. The first one was the conductivity of the working fluid and the surrounding vessel. Electrifying the vessel would be potential dangerous, as hydrogen could form on the inner wall, directly contributing to hydrogen embrittlement and compromising the system. One initial solution was to coat the inside

of the pressure vessel with a nonconductive surface. This seemed like the easiest solution, but ignored the fact that every part of the system, including the inner diameter of the 1/8" stainless steel tubing, needed to be coated as well. The next thought was to use semi-permeable membranes to isolate the conductive water in the pressure vessel and then coat the inside. When the membranes were tested, however, they were unable to handle the pressure difference required for the working fluid to pass through and were dubious in structure when gas was pushed through. Eventually, the sub-vessel idea was tested and worked under pressure conditions, but its creation and design propagated larger problems.

The key element to the design of the sub-vessel was the selection of materials. Several materials, from plastics to polymers, were considered for the sub-vessel container. The material needed to be flexible enough to compress slightly under the high pressures and nonconductive to isolate the electrical system. On top of this, the selected container needed the correct dimensions to fit within the pressure vessel, hold enough working fluid to create a measurable amount of hydrogen, and not move during electrolysis. Many containers were bought and tested and the oval container ended up suiting the best needs. The container itself does not quite fit all the requirements perfectly, as PET hardens when molded into hard corners, but was considered replaceable enough to simply purchase in bulk and replace when necessary. With the

container chosen and suitable, the next step was to find an appropriate top to seal it with.

When sealing the sub-vessel, two important ideas were kept in mind. First, the sealing cap needed enough volume to allow a threaded fitting through. This meant that most thin screw-on caps, like the ones with liners provided, did not have the bulk for inputs to be properly secured. The second, more obvious, criterion was that it needed to seal the working fluid in. The first solution was to use the liners provided and to attach some plastic mass to its top, giving the bulk needed. This proved ineffective, as the plastic did not seal well with the required inputs. The sealing issue led to the use of the rubber stopper, as one could easily be drilled into for inputs while maintaining a good seal on them.

Once the sub-vessel was sealed and working under pressure, the choice of electrodes to carry out electrolysis was the final step. Initially, copper was tried to test the rates of electrolysis. After a couple of tests with copper, it was found that the copper would corrode rapidly and enter solution, impeding further hydrogen production and polluting the water. After some research, two different electrodes were tested: 316 stainless steel and carbon paper. Stainless steel was known for its high resistance to corrosion and ability to last after several experiments, whereas carbon would be essentially inert during electrolysis. After testing both, 316 stainless steel was chosen, as

it was easy to acquire, flexible and machinable, and different meshes could be tested against each other.

After these many hurdles, the system was tested as a whole to see if it held pressure at 5000 psi without any hydrogen production. At this pressure, a few new issues arose. Large gaps in the pressure vessel at the electrode input and output trapped air inside the system, making the pressurization process less efficient and working the pump harder than necessary. This issue was resolved by making the plastic around the electrode larger in the pressure vessel to the point of an interference fit. This eliminated the unreachable gaps and reduced pressurization time. In addition, a few pinhole leaks that were not present at lower pressures presented themselves. These leaks were addressed with ease by adding pressure to the connections and adding silicon sealant to the bigger leaks. Once the pressure vessel was deemed safe and secure at 5000 psi, the sub-vessel was connected and added and electrolysis was started in the system.

5.2 Hydrogen production

While this thesis focuses on the construction and safety of high pressure systems, the creation of hydrogen in this system gives relevance to its creation. Therefore, for the purpose of this thesis, some baseline experiments were carried out to show its effectiveness of producing high-pressure hydrogen. The system was tested at lower pressures before testing at the maximum pressure, ensuring the addition of hydrogen

would not cause additional problems and the system was safe from leaks of potentially harmful product gases.

5.2.1 Hydrogen production specifications

Hydrogen production under 5000 psi occurred under the following conditions. From our power source, the voltage was set at 40 V and compliance 1 A. While running at higher voltages is less efficient than inputting just above the reaction potential, it produces hydrogen at a faster rate. The goal of this experiment was to test the efficacy of the pressurizing system, so higher production rates were more suitable for this type of testing. The pressurizing fluid was distilled water for its isolative properties. Water from the laboratory faucets was used as the working fluid. Tap water was chosen over the designed salt water as the working fluid due to some potential issues of salt water electrolysis. These issues include the production of chlorine gas from electrolysis and the high corrosivity of salt water. Tap water served as an acceptable substitute due to its low amounts of interfering chemicals while still being conductive. According to Durham water reports, the tap water contained normal amounts fluoride, chlorine, sodium and sulfates, with trace amounts of lead and copper (City of Durham, 2012). For the sub-vessel electrodes, two 316 stainless steel mesh rectangles were used for hydrogen generation. These rectangles were cut four centimeters by five centimeters, giving a projected surface area of 20 square centimeters for each one. Modifying the projected surface area to account for the mesh gaps, the actual surface area is closer to 56

square centimeters for #60 mesh (Zhang, Merrill, & Logan, 2010). The separation between the two electrodes averaged to an estimated two centimeters.

5.2.2 Test procedure and results of high-pressure hydrogen generation

With these parameters, the vessel was taken to pressure and electrolysis was initiated. Electrolysis was done for an hour under the given circumstances. Over the course of the experiment, the actual current running through the system fluctuated with time. As shown in Figure 14, the current starts at around 25 mA/cm^2 and slowly levels off over the hour duration.

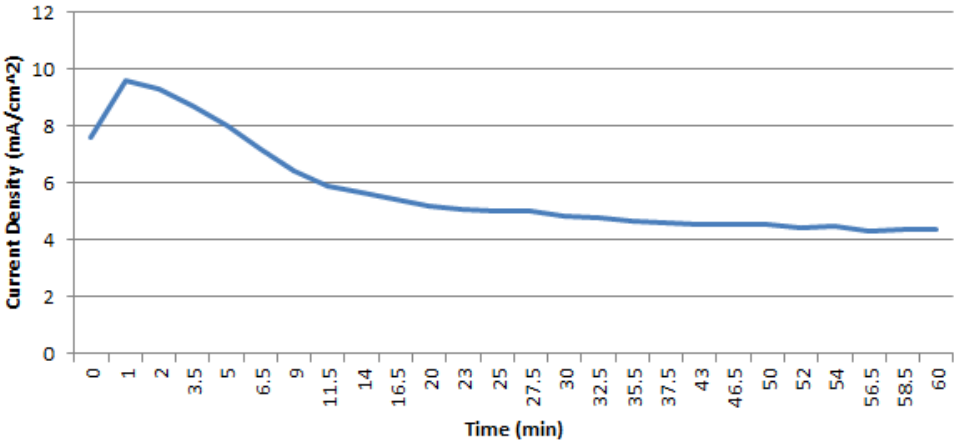

Figure 14: Experimental data from 5000 psi electrolysis.

The hydrogen was released after the hour of electrolysis. There were no hydrogen leaks during any phase of the experiment, showing that hydrogen had been produced under 5000 psi safely. Once released from the ball valve, the gas-water mixture was bubbled through a vacuumed container filled with tap water. From there, the gas was drawn from the container into a syringe to measure the amount of gas

produced. In the experiment done, about 200 ml of gas was produced. Via a hydrogen monitor, this gas was shown to have hydrogen in it. In the ideal experiment, the gas would then be analyzed in a gas chromatograph. However, the gas chromatograph available for use needed a larger amount of gas to analyze the composition of the gas. In lieu of this, assuming that the added impurities of the water reacted minimally and an ideal reaction, it can be computed from the reaction equation that 2/3 of the gas is hydrogen, so roughly 135 ml. These results show that not only was hydrogen produced safely under 5000 psi, but also was produced at the reasonable rate of 2.25 ml/min.

5.3 Conclusions

Despite the end result, there are still several ways the system could be improved. Continuous production would allow for flow out of the system to be controlled and measured, giving better comparisons for the amount of energy it takes to produce hydrogen at a given rate. This continuous production would also make analyzing the components of the output gas easier, as continuous production is not limited to the amount of hydrogen it can produce in a single experiment. As discussed before, if the corrosion and chlorine gas issues can be resolved, the use of sea water would greatly increase the efficiency of the system with low to no cost. Many components will need replacing over depressurizations, as the constant set up and tear down required for a single experiment wear the system at an accelerated rate. If addressed, these issues could greatly improve the practicality and efficiency of a high-pressure electrolysis

system. While these improvements are being made, the concept of producing hydrogen at high pressure has been shown. Although it took a year to assemble, analyze, reassemble and refine the system into what it is now, the time has shown its worth. The system is both safe and secure, laying the foundation for further research into the potentials of high-pressure electrolysis.

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